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A wave packet Golden Rule treatment of vibrational predissociation

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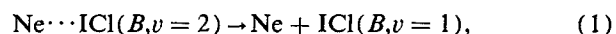
The time-dependent wave packet technique is applied to the Golden Rule treatment of vibrational predissociation. The wave packet at time zero is taken as the product of the quasibound wave function and the coupling inducing predissociation. The rate for vibrational predissociation can then be obtained by Fourier transform into the energy domain of the time-dependent wave packet autocorrelation function. The method has been applied to a model triatomic van der Waals molecule. It is shown that when the bound-state components of the wave packet are projected out, the time-dependent version of the Golden Rule approximation provides an alternative efficient technique to treat intramolecular decay.

I. INTRODUCTION

Vibrational predissociation is an important and basic process of intramolecular energy flow in polyatomic systems. In the last few years many studies have been devoted to vibrational predissociation in van der Waals molecules, in particular for $X \cdots BC$ systems where X is a rare-gas atom and BC an ordinary diatomic molecule.¹ From the theoretical point of view, van der Waals molecules provide ideal examples of coupled oscillators that can be studied in detail both classically and quantum mechanically. For some of the triatomic molecules, numerically converged calculations of vibrational predissociation rates taking into account the three degrees of freedom have been performed by time-independent² as well as by time-dependent wave packet techniques.³ For larger systems the full quantum mechanical approaches are very difficult to implement and approximate methods have to be used. Since there is a natural separation between the fast intramolecular vibrations of the monomers and the slow vibrational modes of the intermolecular van der Waals bond, perturbation theory applied to the fast vibrational modes is usually a very good approximation. In addition, since vibrational predissociation lifetimes are usually much longer than all the vibrational periods in the molecule, the quasibound levels are well isolated and the Fermi's Golden Rule approximation is adequate.^{2(d),4} As for rotation, the infinite-order sudden approximation (RIOSA) has been shown to give accurate results for these systems.^{2e}

Fermi Golden Rule as well as RIOSA have been applied to several van der Waals systems by the use of the time-independent quantum theory.⁵ They can also be implemented in the time-dependent wave packet approach using the same techniques as those used to treat optical lineshapes and Raman spectra.⁶ The interest in using the wave packet version of the Golden Rule treatment is that the propagation over time will presumably have to be carried out for much

shorter periods of time as compared to a full three-dimensional wave packet treatment. Vibrational predissociation lifetimes in van der Waals molecules are usually of the order of tens or hundreds of picoseconds and in some cases much longer. A wave packet approach without approximations will then have to propagate in time for an interval of the order of the lifetime (which implies thousands of the monomer vibrational periods). Hence, very few studies of vibrational predissociation have been performed by this method.^{3,7} On the other hand, the wave packet Golden Rule treatment involves propagation during the dissociation on the final state only, i.e., for a tenth of a picosecond or so. It is the purpose of this paper to present a simple example of this approach. The system chosen is the $Ne \cdots ICl$ complex undergoing the vibrational predissociation process



for which time-independent quantum mechanical results are available.^{2(e)} We show that once the contribution of the bound states of the final dissociative surface is projected out, the wave packet propagation technique in conjunction with the Golden Rule approximation can be an alternative efficient method to treat slow intramolecular decay.

II. THE TIME-DEPENDENT WAVE PACKET APPROACH OF THE GOLDEN RULE

In the framework of the Golden Rule approximation for predissociation, an initial well-isolated bound state ϕ_i of energy E_i decays to a final continuum ϕ_{fE} through a coupling V . The associated lifetime τ is then given by $\tau = \hbar/2\Gamma(E_i)$ with⁴

$$\Gamma(E) = \pi |\langle \phi_i | V | \phi_{fE} \rangle|^2 \quad (2)$$

being the half-width associated to predissociation lineshapes. Equation (2) can also be written as

$$\begin{aligned}\Gamma(E) &= \pi \int dE' |\langle \phi_i | V | \phi_{fE'} \rangle|^2 \delta(E' - E) \\ &= \frac{1}{2\hbar} \int dE' |\langle \phi_i | V | \phi_{fE'} \rangle|^2 \int_{-\infty}^{\infty} dt e^{-i(E' - E)t/\hbar},\end{aligned}\quad (3)$$

where the integral representation of the δ function has been used to obtain the second equality. Equation (3) can be transformed to

$$\begin{aligned}\Gamma(E) &= \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} \\ &\quad \times \int dE' \langle \phi_i | V e^{-iH_f t/\hbar} | \phi_{fE'} \rangle \langle \phi_{fE'} | V | \phi_i \rangle,\end{aligned}\quad (4)$$

where H_f is the Hamiltonian acting in the final subspace $|f\rangle$. Denoting by $\phi_{f\beta}$ the discrete eigenfunctions of H_f with energies $E_{f\beta}$, we have the closure relation for the subspace $|f\rangle$

$$\sum_{\beta} |\phi_{f\beta}\rangle \langle \phi_{f\beta}| + \int dE' |\phi_{fE'}\rangle \langle \phi_{fE'}| = 1,\quad (5)$$

which after introduction into Eq. (4) produces

$$\begin{aligned}\Gamma(E) &= \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} [\langle \Phi(0) | \Phi(t) \rangle \\ &\quad - \langle \Phi(0) | \Phi_b(t) \rangle],\end{aligned}\quad (6)$$

where we have defined

$$|\Phi(0)\rangle = V |\phi_i\rangle, \quad |\Phi(t)\rangle = e^{-iH_f t/\hbar} |\Phi(0)\rangle\quad (7)$$

and

$$\begin{aligned}|\Phi_b(0)\rangle &= \sum_{\beta} |\phi_{f\beta}\rangle \langle \phi_{f\beta} | \Phi(0)\rangle, \\ |\Phi_b(t)\rangle &= e^{-iH_f t/\hbar} |\Phi_b(0)\rangle.\end{aligned}\quad (8)$$

Thus $|\Phi(0)\rangle$ is a wave packet obtained by multiplication of the initial quasibound eigenfunction $|\phi_i\rangle$ by the coupling V between the initial and final channels. On the other hand, $|\Phi_b(0)\rangle$ is the projection of $|\Phi(0)\rangle$ onto the bound eigenfunctions $|\phi_{f\beta}\rangle$ of the final state. Similarly, we can define the projection onto the continuum eigenstates $|\phi_{fE'}\rangle$ by

$$|\Phi_c\rangle = \int dE' |\phi_{fE'}\rangle \langle \phi_{fE'} | \Phi \rangle = |\Phi\rangle - |\Phi_b\rangle.\quad (9)$$

Using Eqs. (8) and (9) into Eq. (6) we finally get

$$\begin{aligned}\Gamma(E) &= \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} \langle \Phi(0) | \Phi_c(t) \rangle \\ &= \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} \langle \Phi_c(0) | \Phi_c(t) \rangle,\end{aligned}\quad (10)$$

which shows that $\Gamma(E)$ is the Fourier transform of the auto-correlation function $\langle \Phi_c(0) | \Phi_c(t) \rangle$, where $\Phi_c(0)$ is the projection of the initial wave packet $|\Phi(0)\rangle = V |\phi_i\rangle$ onto the continuum spectrum of the final dissociative channel.

III. APPLICATION TO VIBRATIONAL PREDISSOCIATION OF A VAN DER WAALS COMPLEX

We have applied the time-dependent wave packet approach of the Golden Rule approximation to the vibrational predissociation of $\text{Ne} \cdots \text{ICl}$ as described by Eq. (1). We first

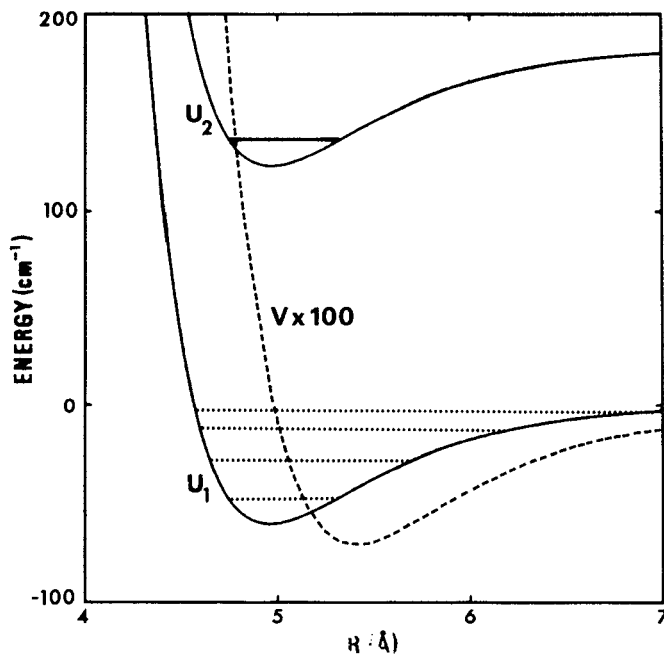


FIG. 1. Potential energy curves and coupling used in the model calculations presented in this work.

define the initial and final channels. This is achieved by separating out the fast vibrational motion of ICl from the other modes of the complex. Denoting by $\chi_v(r)$ the vibrational eigenfunctions of ICl, we define the channel potentials by $U_v = \langle \chi_v | H | \chi_v \rangle$. In our model calculation the initial and final channels correspond to the $v = 2$ and $v = 1$ vibrational states of $\text{ICl}(B)$, respectively. The coupling responsible for predissociation is then given by $V = \langle \chi_2 | H | \chi_1 \rangle$.

The calculations presented in this work have been performed for a fixed angular configuration corresponding to the equilibrium geometry of the complex ($\theta_e = 140^\circ$). Therefore, U_1 , U_2 , and V depend only on the distance R between the Ne atom and the center of mass of the ICl molecule. They are represented in Fig. 1 for the intermolecular potential parameters of Ref. 2(e).

The initial wave function ϕ_i corresponds to the zero-point level of the U_2 vibrational channel (see Fig. 1). The initial wave function ϕ_i as well as the wave packet $\Phi(0) = V \phi_i$ are represented in Fig. 2 as a function of R . Since the coupling V changes sign in the region of the well (a property which is common to all van der Waals interactions constructed as a sum of atom-atom pairwise potentials), $\Phi(0)$ has a node in that region.

In the first channel, which corresponds asymptotically to $\text{Ne} + \text{ICl}(B, v = 1)$, there are four bound levels (see Fig. 1). The wave packet $\Phi(0)$ has a substantial projection on those levels. After calculation of the bound levels using a Numerov algorithm, we have found that

$$\langle \Phi_b(0) | \Phi_b(0) \rangle = 0.766 \langle \Phi(0) | \Phi(0) \rangle.\quad (11)$$

We have also found that the square of the projection $|\langle \phi_{f\beta} | \Phi(0) \rangle|^2$ onto the van der Waals levels $l = 1$ and $l = 2$ amounts for 0.47 and 0.22, respectively, with very small components on the other levels. After subtraction of the pro-

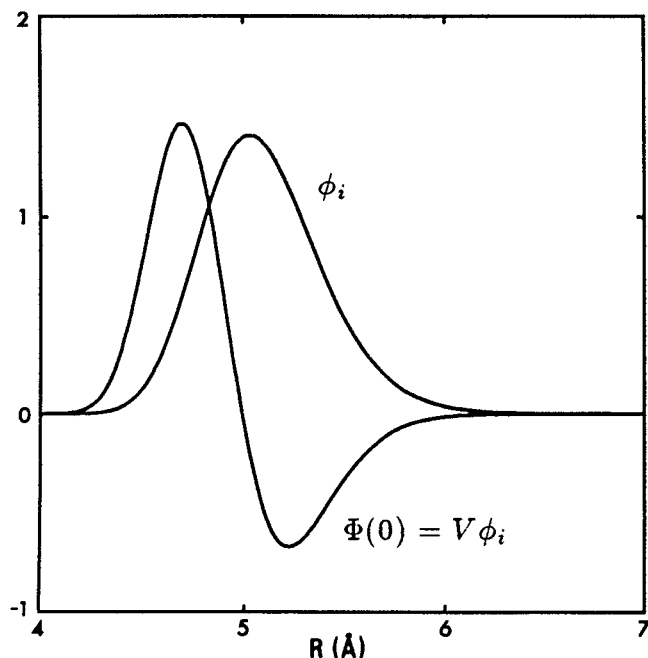


FIG. 2. Initial wave function ϕ_i and wave packet $\Phi(0) = V\phi_i$. The units are $(\text{\AA}^{-1/2})$ for ϕ_i , and $[\text{cm}^{-1}\text{\AA}^{-1/2}]$ for $\Phi(0)$.

jection onto the bound levels $|\phi_n\rangle$ according to Eq. (9), we obtain the "continuum" wave packet $|\Phi_c(0)\rangle$ which is represented in Fig. 3.

We now turn to the actual propagation in time of the wave packet. The time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Phi}{\partial t} = H_f \Phi(t) \quad (12)$$

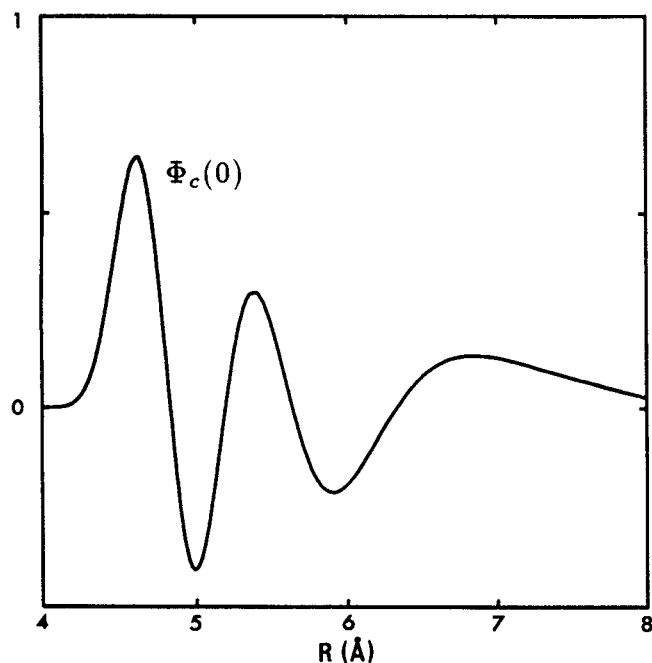


FIG. 3. The "continuum" wave packet $\phi_c(0)$ obtained by subtracting to $\Phi(0)$ the projection onto the van der Waals bound levels of the final channel. Units are $(\text{cm}^{-1}\text{\AA}^{-1/2})$.

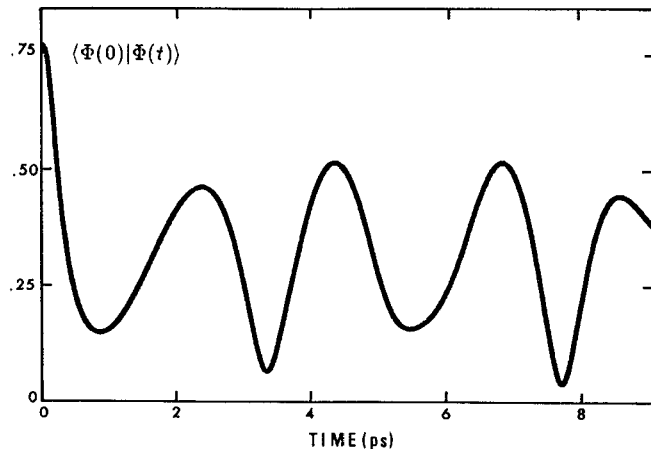


FIG. 4. Absolute value of the autocorrelation function $\langle \Phi(0)|\Phi(t) \rangle$. Units are $(\text{cm}^{-1})^2$.

is solved by a five-point Runge-Kutta-Gill plus an Adams-Moulton integrator with time steps of 10^{-16} s. The H_f Hamiltonian in our case is

$$H_f = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + U_1(R). \quad (13)$$

The action of H_f on the wave packet has been calculated by finite differences on a grid of 1024 points from 0 to 12 \AA . This provides well-converged results. The accuracy of the results has also been checked by Fourier transform instead of finite differences. Since we had a very fine mesh, there were no advantages of using one or the other of the two methods. For problems involving several degrees of freedom the Fourier transform should be preferred in order to reduce the number of grid points. In Fig. 4 we present the absolute value of the autocorrelation function $|\langle \Phi(0)|\Phi(t) \rangle|$ as a function of time for a time interval of the order of 10 ps. It is seen that after a short-time decay of the order of 0.2 ps, oscillations appear that are not damped. This corresponds to the evolution in time of the bound states components of the wave packet. On the other hand (see Fig. 5), if the projected wave packet $|\Phi_c\rangle$ is propagated in time the autocorrelation function $\langle \Phi_c(0)|\Phi_c(t) \rangle$ decays monotonically to zero in a time

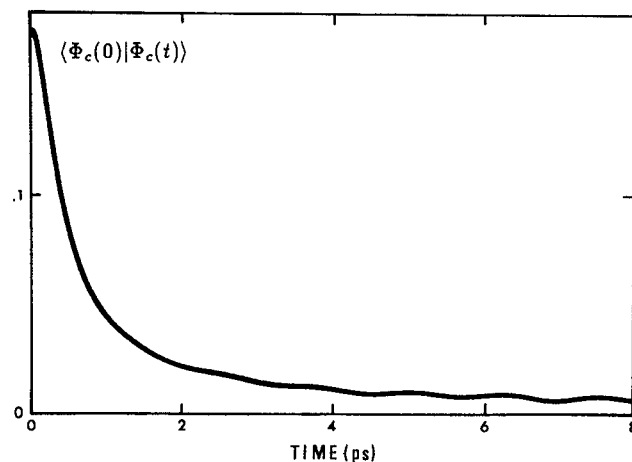


FIG. 5. Same as Fig. 4 for $\langle \Phi_c(0)|\Phi_c(t) \rangle$.

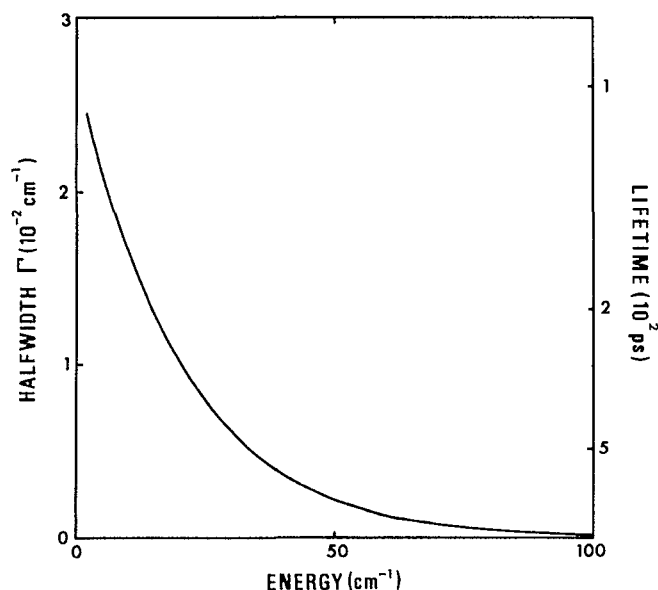


FIG. 6. Half-width Γ and lifetime as a function of energy obtained by Fourier transform of $\langle \Phi_c(0) | \Phi_c(t) \rangle$.

scale of less than a picosecond. After performing the Fourier transform of $\langle \Phi_c(0) | \Phi_c(t) \rangle$ we obtain in accordance to Eq. (10) the half-width $\Gamma(E)$. The result is presented in Fig. 6. The results are in perfect agreement with those obtained by a time-independent quantum mechanical calculation using Eq. (2), for all energies between five and several thousands wave numbers. Since the autocorrelation function is calculated only up to about 8 ps, the Fourier transform gives accurate results only for frequencies larger than $2\pi/8(\text{ps})^{-1}$. This corresponds to energies above 4 cm^{-1} . On the other hand, as the integration step is 10^{-16} s , the upper limit is $3 \times 10^5 \text{ cm}^{-1}$. Only a small fraction of the total Fourier transform is presented in Fig. 6. It should be noted at this point that in the usual case of predissociation the energy E_i of the initial state ϕ_i is fixed, and the Golden Rule specifies that the halfwidth $\Gamma(E)$ has to be evaluated at $E = E_i$.

This example shows clearly the advantage of using the Golden Rule approximation. Predissociation lifetimes (see Fig. 6) range from ten to several hundreds of picoseconds. Hence a full time-dependent treatment taking into account all degrees of freedom will have to integrate in time for many thousands of ICl vibrational periods. On the other hand, in the time-dependent wave packet approach of the Golden Rule approximation the autocorrelation function for the projected wave packet $|\Phi_c\rangle$ decays in less than a picosecond, making the calculation much less expensive.

IV. CONCLUSIONS

In this paper we have shown the feasibility of extracting lifetimes of metastable species such as electronically excited van der Waals complexes via time-dependent wave packet techniques. Rather than simulate the decay dynamics directly, which is difficult because of the long time scales involved, we rely on the Golden Rule approximation that prescribes an approximate lifetime in terms of quantities that are much

easier to calculate. For van der Waals triatomics the Golden Rule is known to give very good results when the energy level spacings are much larger than the half-width Γ of the resonances. This is the case for many systems, including $\text{Ne} \cdots \text{ICl}$, the molecule featured in this paper.

The Golden Rule has been utilized previously to investigate decay of van der Waals complexes. The novel feature of the present work is a transcription of this recipe into the time domain. The computational burden is thereby shifted from determining continuum eigenfunctions for a prescribed potential energy surface to propagating wave packets on the same surface. The time-domain approach of the Golden Rule approximations appears naturally suited for computing decay lifetimes because only short time wave packet dynamics is required. Moreover, this dynamics is simple in the sense that the autocorrelation function $\langle \Phi_c(0) | \Phi_c(t) \rangle$ derived from it exhibits simple monotonic decay. In future work we hope to exploit this feature to compute lifetimes for tetraatomic and larger systems, for which frequency-domain approaches (even in the Golden Rule approximation) are not currently feasible. Interesting candidates for this type of study include the $\text{HF} \cdots \text{HF}$ dimer and Ne_2Cl_2 . The idea is that propagating on the effective coupled channel potential curves resulting from the separation of the high-frequency vibrations of the monomers, will still be of the "short-time" type. The propagation can then be accomplished via a number of techniques such as Gaussian wave packet, time-dependent Hartree-grid wave packet or even Monte-Carlo path integration, which are known to be both implementable and accurate for many-body dynamics of this type.

¹ For a review see, K. C. Janda and C. R. Bieler in *Atomic and Molecular Clusters* edited by E. R. Bernstein (Elsevier, Amsterdam, 1990).

² (a) J. M. Huston, C. J. Ashton, and R. J. Le Roy, *J. Phys. Chem.* **87**, 2713 (1983); (b) J. M. Hutson, *J. Chem. Phys.* **81**, 2357 (1984); (c) I. F. Kidd and G. Balint-Kurti, *ibid.* **82**, 93 (1985); (d) N. Halberstadt, J. A. Beswick, and K. C. Janda *ibid.* **87**, 3966 (1987); (e) O. Roncero, J. A. Beswick, N. Halberstadt, P. Villarreal, and G. Delgado-Barrio, *ibid.* **92**, 3348 (1990).

³ (a) S. K. Gray and C. E. Wozny, *J. Chem. Phys.* **91**, 7671 (1989); (b) S. K. Gray and C. E. Wozny, *J. Chem. Phys.* (in press).

⁴ (a) J. A. Beswick and J. Jortner, *Adv. Chem. Phys.* **47**, 363 (1981); (b) R. J. Le Roy, in *Resonances in Electron-Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics*, edited by D. G. Truhlar (A.C.S. Symposium Series, No. 263, American Chemical Society, Washington, DC, 1984).

⁵ (a) J. A. Beswick and G. Delgado-Barrio, *J. Chem. Phys.* **73**, 3653 (1980); (b) E. Segev and M. Shapiro *ibid.* **78**, 4969 (1983); (c) N. Halberstadt, O. Roncero and J. A. Beswick, *J. Chem. Phys.* **129**, 83 (1989); (d) R. L. Waterland, M. I. Lester, and N. Halberstadt, *J. Chem. Phys.* **92**, 4261 (1990).

⁶ (a) K. C. Kulander and E. J. Heller, *J. Chem. Phys.* **69**, 2439 (1978); (b) S. Y. Lee and E. J. Heller, *ibid.* **76**, 3035 (1982); (c) R. H. Bisseling, R. Kosloff, and J. Manz, *ibid.* **83**, 993 (1985); (d) R. D. Coalson, *Chem. Phys. Lett.* **147**, 208 (1988); (e) S. O. Williams and D. G. Imre, *J. Phys. Chem.* **92**, 6648 (1988); (f) J. Zhang, D. G. Imre, and J. H. Frederick, *ibid.* **93**, 1840 (1989); (g) X. P. Jiang, R. Heather, and H. Metiu, *J. Chem. Phys.* **90**, 2555 (1989); (h) M. Jacon, O. Atabek, and C. Leforestier, *ibid.* **91**, 1585 (1989).

⁷ (a) R. Viswanathan, L. M. Raff, and D. L. Thompson, *J. Chem. Phys.* **77**, 3939 (1982); (b) L. L. Halcomb and D. J. Diestler, *ibid.* **84**, 3130 (1986); (c) S. K. Gray, *ibid.* **87**, 2051 (1987); (d) R. H. Bisseling, R. Kosloff, R. B. Gerber, M. A. Ratner, L. Gibson, and C. Cerjan *ibid.* **87**, 2760 (1987).